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Unravelling Radicals Reactivity Towards Carbon Nanotubes Manipulation/Functionalization

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Abstract: Carbon Nanotubes (CNTs) chemistry is under constant evolution, as a consequence of the deep interest of the scientific community in finding new applications for these versatile materials. New and old synthetic protocols are used for improving the control of the functionalization degree of the final materials and for offering to scientists the possibility to fine-tune their final properties. In this Review, we focus the attention on radical reactions, a class of protocols characterized by small number of steps, different degrees of functionalization and enhanced solubility of the final modified CNTs, in the desired environment. The most well-known protocols are analysed providing some relevant examples appeared in the literature in the last years, monitoring the new application fields and giving insights into their mechanism in order to explain why these protocols are considered standard procedures for a wide number of scientific groups.

Keywords: Carbon Nanotubes, radicals, carboxylation, diazonium salts, Birch reduction, epoxidation, polymer grafting.

INTRODUCTION

Carbon Nanotubes (CNTs) appear to be one of the most promising substrates of the last decades and of the near future because of their several features which make them very useful for the construction of novel hybrid materials [1]. Since the first observations of Single-Walled Carbon Nanotubes from Iijima *et al*., [2] the interest around this allotropic form of carbon constantly grew up. Their tubular structure consists of one (Single-Walled Carbon Nanotubes, SWCNTs), two (Double-Walled Carbon Nanotubes, DWCNTs) or more (Multi-Walled Carbon Nanotubes, MWCNTs) layers of sp^2-hybridized carbon atoms organized in a fully conjugated lattice. CNTs exhibit many extraordinary properties and show to be promising for several applications, including electronics [3], gas storage [4], catalysis [5], and high-performance composites [6]. The robustness and mechanic resistance of these materials are already well employed for the production of reinforced polymeric materials [7], while the highly conjugated atomic network confers outstanding electronic properties which has made possible their integration in LEDs, FETs, and materials for sensor technology [8]. Moreover, CNTs biocompatibility and their peculiar mechanisms of inclusions in cells open the way to innovative drug delivery systems in which they act as drug carrier [9].

So far and despite the abovementioned achievements, CNTs can be produced only in mixtures of different length, diameter and chirality species. This appears as a bottleneck for their use in nanodimensioned devices. Another major obstacle is their insolubility in the most of the solvents which is mainly due to their strong *van der Waals* interactions, leading to bundling and aggregation phenomena of this novel carbon material [10]. Therefore, the ultimate objective would be to isolate nanotubes consisting only of monodispersed population of tubes in terms of chirality and diameter with improved solubility properties and suitable for the grafting with a large variety of different compounds [11].

The chemical substitution of the scaffold of CNTs is among the purposed strategies to overcome these obstacles [12]. In order to open the way to industrial and large-scale applications, many attempts of CNTs chemical functionalization are reported [13]; most of them point out their attention on the disruption of aggregates and bundles. Albeit the progresses which have been made in the last ten years, many efforts are still needed for improving CNTs manipulation. The main approaches for modifying CNTs can be categorized in two groups: (a) the non-covalent interaction of specific surfactants [14] and (ii) the covalent attachment of organic/inorganic pendants [15]. The former approach produces nanotubes with unchanged chemical and physical properties surrounded by a shell of surfactant molecules, like primarily surfactants [16], biomacromolecules [17] or polymers [18]. In these cases the strength of the interaction of CNTs with these molecules is relatively low. Accordingly, the covalent functionalization of SWCNTs has become the subject of extensive research within the last ten years [19]. In addition, the exploration of the chemistry of carbon nanotubes is of academic interest as their reactivity can be directly related to the reactivity of the other molecular carbon allotropes. In comparison to their closest relatives, *e.g.* 1D fullerenes and 2D graphene, the reactivity of carbon nanotubes is governed by two factors: curvature-induced pyramidalization of individual carbon atoms and π-orbital inappropriate alignment between adjoining pairs of carbon atoms [20]. Thus, the reactivity can be, in general, ranked between fullerenes with highest reactivity and graphene exhibiting much lower reactivity. As a consequence, small diameter nanotubes are anticipated with higher reactivity than the larger ones. However, the in-depth exploration of the direct sidewall derivatization of SWCNTs has clearly shown that their reactivity towards additional reactions is considerably less pronounced than the one of classical molecules involving a conjugated π-system. Therefore, the chemist's toolkit for the structural framework alteration of CNTs is pre-

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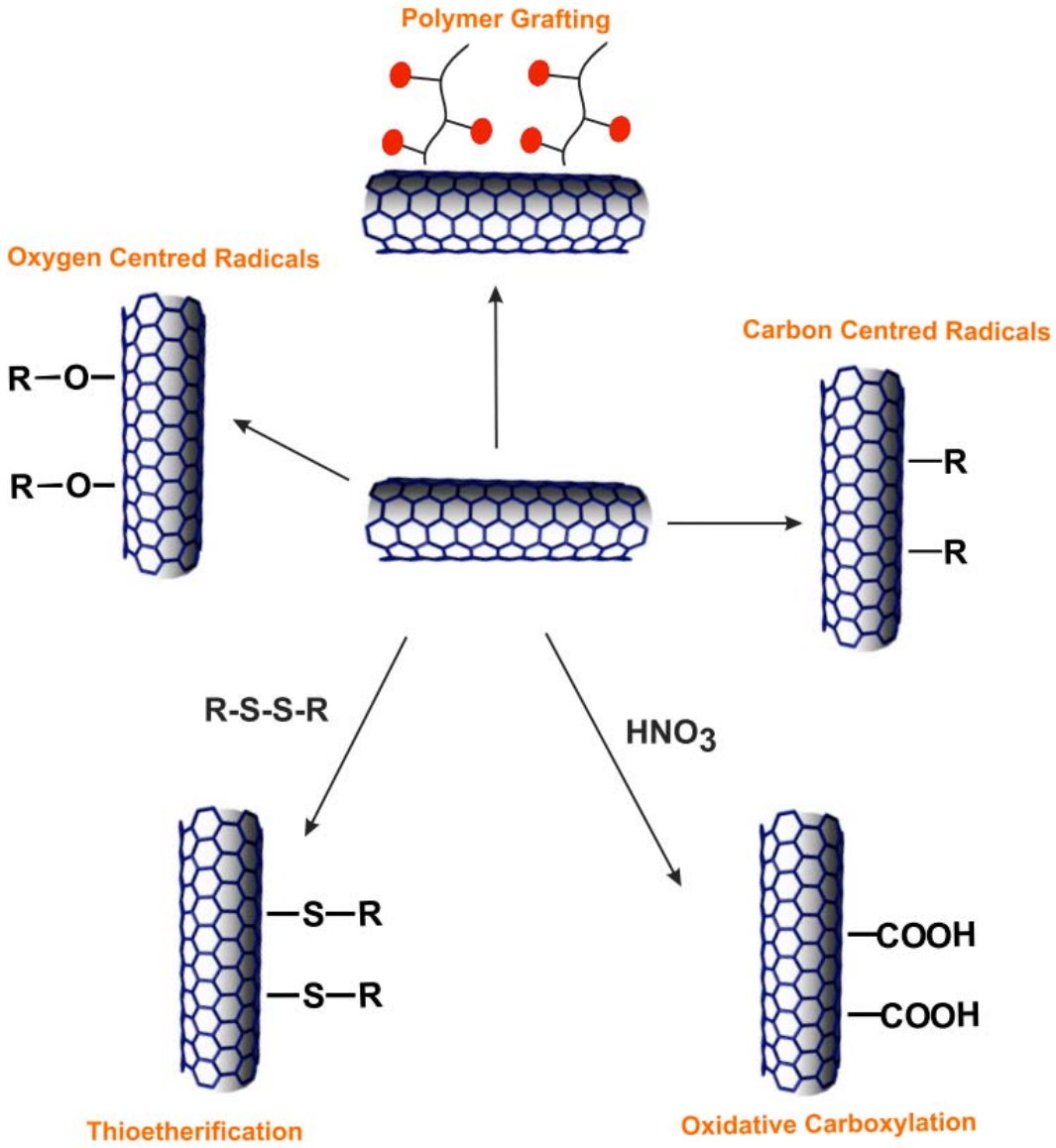

Fig. (1). Schematic representation of the radical functionalization protocols discussed in the Review.

dominantly limited to comparatively harsh reaction conditions and very reactive intermediates [21]. Among them, the one that is used more often is the radical compounds. CNTs can be functionalized by radical species as fullerenes can be [22]. This is an interesting approach because it offers an easy tool for performing large-scale functionalization and providing tubes with moieties prompt to further elaboration. This occurs when the carbonaceous scaffold has to act as nano-carrier for the attachment of molecules with high load level, or when high solubility of the tubes is required. Even if in a general meaning the word "radical" is associated to reactions which are proceeded without control, several protocols have been developed in order to fine-tune the formation of the new chemical bonds.

The variety of developed synthetic pathways guided us for the classification of these reactions in the following categories (Fig. **1**):

1. Carboxylation reactions
2. Oxygen Centred Radicals
3. Carbon Centred Radicals (diazonium salts, Birch reduction, carbene addition)
4. Disulfides
5. Polymer grafting

1. CARBOXYLATION REACTION

Carboxylation reactions are comprehensive of a wide class of reactions which allow the decoration of carbon nanotubes surface with carboxylic motif. These reactions are usually exploited for different aims. Mainly, they can be useful (i) for the formation of new oxygenated functional groups around the surface of CNTs, providing higher solubility of the nanostructures or (ii) for inserting carboxylic groups as platforms for grafting several moieties [23].

Among reactions for the introduction of -COOH groups, radical oxidation processes are a relevant subclass. In general terms, oxidation treatments involve defects already present over carbon nanotubes' surfaces or the formation of new defective sites promoted by aggressive agents, *i.e.* strong acids [24]. Oxidative processes introduce oxygen-containing functional groups, mainly carboxylic groups but also alcohols and carbonyl moieties could be present in the final material. As a general statement can be said that the more is the strength of the oxidation method, the highest is the population of the oxygenated groups centred over -COOH moieties [25].

Oxidation is absolutely one of the first procedures which were used for the functionalization of CNTs (MWCNTs and SWCNTs, respectively) [23a, 26]. Preliminary works were focused on the introduction of carboxylic moieties on the cutting open-edge of CNTs upon treatment with HNO_3/H_2SO_4 mixture [27]. Lately, Zhang *et al.* [28] reported a study on the chemical oxidation on the scaffold of single-walled carbon nanotubes (SWCNTs) with the use of a variety of oxidant agents. Among the latters, HNO_3 (2.6 M), a concentrated H_2SO_4 - HNO_3 (v/v = 3/1) mixture and $KMnO_4$ were tested. The results revealed that a varying amount of chemical groups can be attached treating SWCNTs with different oxidant agents. For instance, leading the reaction in dilute HNO_3 at reflux, a mild oxidation procedure for SWCNTs, carboxylic acid groups can be selectively inserted in proximity of initial defects already existing on the nanostructure or of the ones generate during nanotubes production process. More recently, Datsyuk and coworkers [25] describe the effects of oxidation on the structural integrity of MWCNTs upon treatments with acidic (HNO_3 and a mixture of H_2SO_4 and H_2O_2) and basic (NH_4OH - H_2O_2) agents. Results clearly show that refluxing CNTs with nitric acid is the most effective oxidative protocol giving the highest degree of degradation, nanotubes shortening and generation on the graphitic scaffold different defects. In general, the oxidative treatment leads to the complete removal of amorphous carbon and metal oxide impurities.

Another work alternatively proposes surface oxidation of SWCNTs using fuming nitric acid as NO_2 radical source for obtaining good solubility in polar solvents [29]. It is also reported that CNTs sonication in H_2SO_4/HNO_3 increase the presence of carboxylic acid groups not only at the preexisted defect sites but also at the produced ones along the walls of CNTs [28].

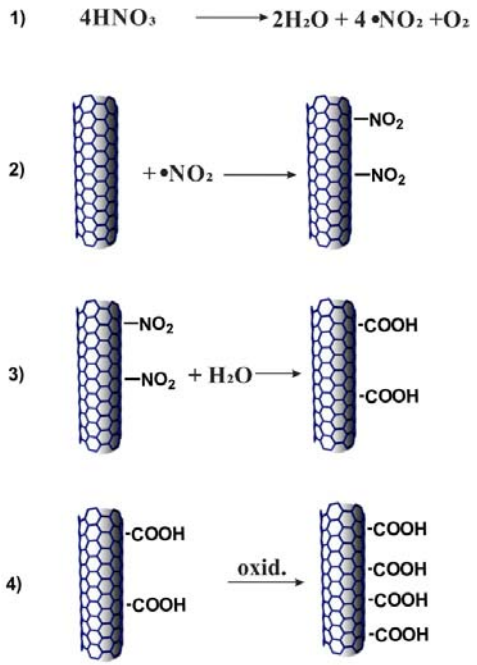

Fig. (2). Proposed reaction mechanism for CNTs surface modification in presence of oxidative environment.

The last two mentioned works aimed to shade light on the mechanism of carboxylation process. The whole process can be described as a 3 steps reaction: (i) the defect-generating step, (ii) defect-stabilization step and (iii) the defect-consuming step (Fig. **2**). In the first phase, the oxidant NO_2 radicals attack the aromatic lattice structure. NO_2 radical is known to be sufficiently reactive toward many olefins and fullerenes [30]. This can explain the importance of pH as reaction parameter, since the presence of an excess of acidic protons in the environment makes the protonation of the oxidative agent possible, followed by its decomposition and the generation of the active radical species. The second step involves a nucleophilic substitution reaction with water molecules, followed by progressive oxidative steps, promoted from the same oxidative environment. Finally, in the course of the defect-consuming step, the carbon scaffold is changed by the oxidation of the newly produced areas. The defect-consuming step is based on the capability of the oxidant to open the honeycomb lattice around the carbon-oxygen bond and their neighbourhood groups.

2. OXYGEN CENTRED RADICALS

CNTs oxidation is a widely followed procedure that has been used to enhance the solubility and chemical reactivity of the sp^2-carbon atoms as we have already referred above. As a consequence, the development of the oxidations' procedures is a challenging scientific subject that at the same time do not alter the morphology of the CNTs [31]. One of the most efficient agents that can oxidize CNTs is ozone (O_3) (Fig. **3**). Its high reactivity towards double bond functional fragment has been extensively described in the literature [32] and can be easily tuned for the nanotubes oxidation processes [33]. First attempts of nanotubes oxidation upon ozone-treatment were performed during investigations of ozone reactivity towards fullerenes and related materials [34]. Lately, Simmons *et al.* [35] demonstrate that O_3 treatments affect the physical and electronic structure of SWCNTs. An additional work on gaseous mixture of ozone and water vapour at room temperature, requiring low concentration and low purity O_3 source, for improving the ozone oxidative conditions, is described in literature [36]. Furthermore, Morales-Lara *et al.* [37] report the selective functionalization of MWCNTs which were treated with ozone in basic solution. In this work, they state that the production of hydroxyl radicals is possible even at basic pH. In general, the oxidative strength of these gas-liquid phase mixtures is pretty high compared to the other protocols. On the other hand, the yield of functionalization that can be achieved in this way is quite low due to the kinetic restrictions of the process.

Interesting applications of ozonolysis reaction has been described. Trancik *et al*. [38] report the use of ozone-oxidized highly catalytic carbon nanotube films, active in the reduction of triiodide (I_3^-). This application is quite relevant, since reduction of I_3^- is an important passage in dye-sensitized solar cells (DSSCs). In the cited paper, authors describe a significant enhancement of the catalytic activity by increasing the degree of functionalization upon ozone treatment. This result opens the way for the use of oxidized nanotube films in the dye-sensitized solar cell devices. Among interesting purposed applications, Byl and coworkers [39] analyse the gas absorption capabilities of ozone-oxidized nanotubes in order to produce porous materials suitable for gaseous species storage. By the means of TEM analysis they highlighted morphological changes in the sample after oxidation treatment; moreover Brunauer-Emmett-Teller (BET) analysis showed the presence of new mesoporosity created from oxidation which can further contribute to gas absorption properties.

Among chemicals that can provide oxygen centred radicals, classical organic peroxides such as 3-chloroperbenzoic acid (*m*-CPBA) [40] easily generated by ultraviolet excitation of molecular oxygen [35], have been extensively used. In 2006, Billups *et al*. [41] demonstrated that oxidizing mixture based on methyltrioxor-

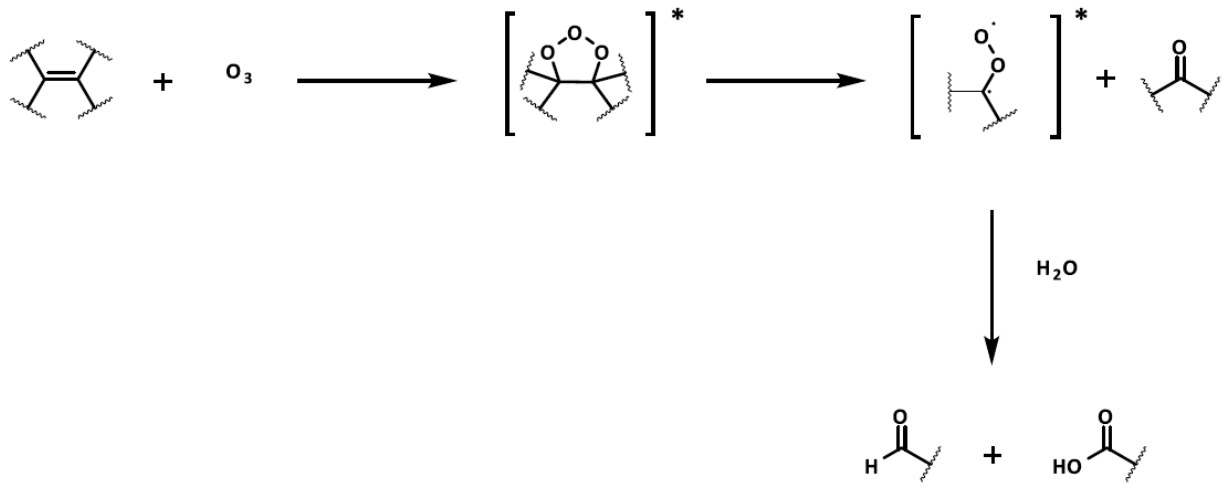

Fig. (3). Reaction mechanism for CNTs ozonolysis.

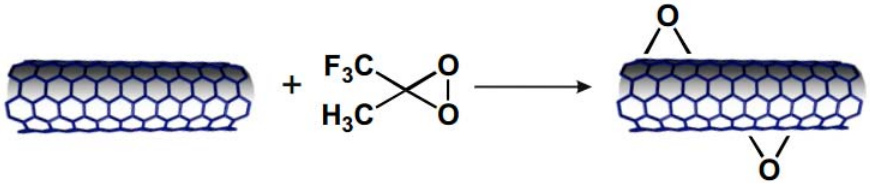

Fig. (4). Schematic representation of epoxidation process over SWCNTs in accordance with the protocol proposed by Annese *et al.* [31].

henium ($ReMeO_3$)/hydrogen peroxide yielded epoxidation of the CNTs. Interestingly, in the same work they purpose that ozonolysis, as well as wet chemical methods, results in epoxidation of the sidewall and they managed to quantify the epoxide content in oxidized SWCNTs, through catalyzed deoxygenation process. More recently, dioxiranes have been theoretical described as viable oxidizing agents for nanostructures [42]. *In situ* preparation method of methyl(trifluoromethyl)di-oxirane (TFDO) [41] and its use has been described, although a lack of strict control of the peroxide concentration during the oxidizing CNTs reaction was observed. Unlike the latter method, the use of isolated TFDO, has been recently reported by Annese *et al.* [31], to allow a simple tuning of the degree of oxidation (Fig. **4**).

Other precursors can be both diacyl and dibenzoyl peroxides, which simply by thermal decomposition straightforwardly produce the requested radical species which quickly and efficiently functionalize the CNTs. Umek *et al.* [43] report the functionalization of SWCNTs by the use of different peroxides with good degrees of functionalization, while McIntosh *et al.* [44] propose an alternative route where the peroxide is employed as initiator and the radical species react in presence of a second reagent (in the specific case polypropylene) operating the final functionalization of nanotubes, in order to constitute a reinforced polymeric matrix. Finally, Ying *et al.* [45] report the use of benzoyl peroxide in the presence of alkyl iodides for the production of free radicals. The radical active species are alkyl groups, and because of their simple attachment to CNTs the solubility is enhanced.

3. CARBON CENTRED RADICALS

3.1. Diazonium Salts

The analogy between carbon nanotubes and fullerenes and aromatic compounds in general from a reactivity point of view opened a new perspective towards other possible approaches to perform functionalization of the CNTs. One example is offered from aryl diazonium salts. These salts are the most popular reagents in the scientific community for increasing CNTs processability, upon functionalization [46]. Preliminary attempts has been performed on different carbon surfaces [47], but Tour *et al.* [48] firstly reported an accurate investigation of the so called "recycled" synthetic approach.

The reaction is a novel application of the *Sandmeyer* reaction, a centennial well-established protocol for the substitution of an aromatic amino functional motif with a nucleophile (*i.e.* an alkene) [49]. Some manipulation is needed before activating the aromatic scaffold towards substitution; the first step consists in the transformation of the aromatic amine in a diazonium salt. The transformation of the functional group occurs in presence of alkyl nitriles or nitride salts. The presence of the diazonium group offers a simple leaving group (N_2) which can be easily replaced from even weak nucleophiles. In basic conditions, the diazonium group gets transformation in a diazotate and in the coupling product, a diazoanhydride (see Fig. **5**); thermolysis is needed for promoting the degradation of this intermediate and generate the aryl radical. This is the electrophile which is finally reacting over the nanotubes surface, even if its high reactivity could promote also some side-reactions. The presence of a reducing agent, such as copper (I) and iron (ll) salts, helps the radical decomposition of the diazonium ones.

After the first paper appeared in 2001 [51], the scientific interest has been focused on a deep analysis of a series of reaction parameters (presence or not of solvent, nature of the solvent, reactivity of the radical agent, etc.) in order to find a correlation between those parameters and the functionalization yield. Among all the results, an interesting work of 2003 pointed out the advantages and disadvantages of reactions led in presence or absence of solvent [52]. It clearly appears that "neat" conditions allow bypassing solvent chemistry, with a simplification of post-process work-up. Moreover, the process can be easily transferred to large-scale production, since it is appeared as a suitable one for applications in the

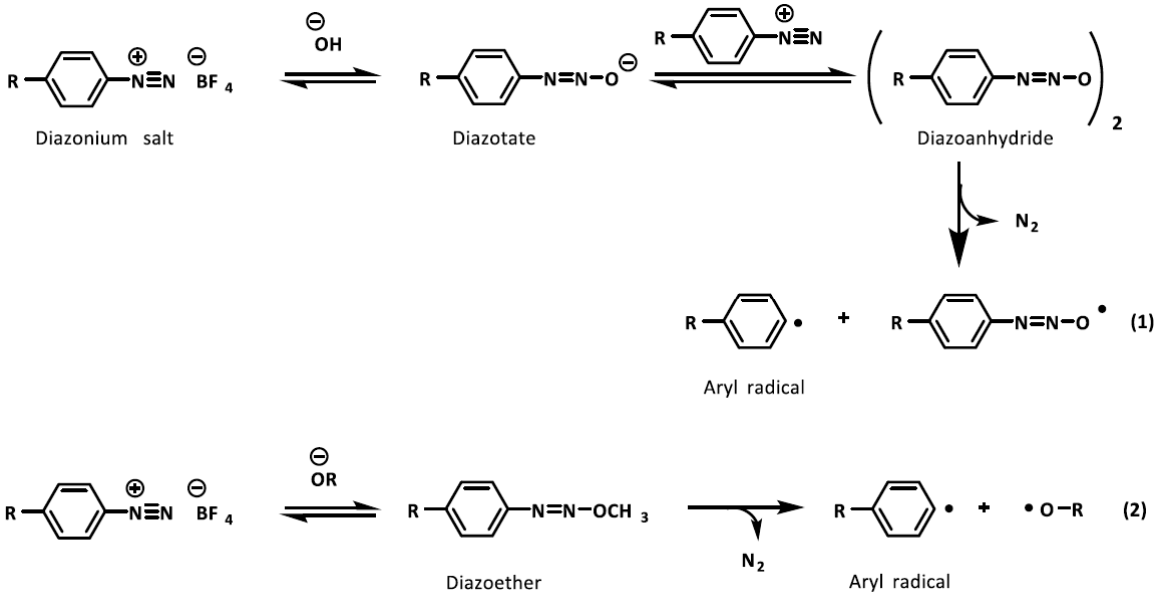

Fig. (5). Typical aryl diazonium salt decomposition pathways (modified from reference [50]).

development of materials. On the other hand, the main disadvantage is intrinsically related to solid state chemistry: nanotubes are strongly aggregated forming bundles and ropes due to their efficient π- π interactions which reduce their reactivity.

Besides the neat condition, there is another one which takes place in aqueous media with the use of surfactants, where the CNTs are firstly being dispersed; then follows their functionalization. The possibility of treating the mixture with ultrasound irradiation and prolonged stirring help pristine nanotubes to start the de-bundling process and provide individual CNTs which can be functionalized in an easier way. This procedure succeeds in high yields of functionalized nanotubes that do not rebundle, giving stable dispersions in organic solvents. This procedure gives materials well dispersed in the solvent of choice, allowing easy further manipulations. The so-conduced modification of the surface allow to deal with materials with uniform behavior and solubility. A further proof of the efficacy of diazonium salts chemistry can be offered by simply measuring the quantity of nanotubes dispersed in a variety of solvents. Tour and Dyke [53] collected results from previous publications and reported solubility values of 0.7 mg/mL in *o*-DCB, 0.8 mg/mL in DMF, and 0.6 mg/mL in chloroform and THF, respectively.

Among the solvents, different mixtures containing H_2SO_4 were tested. Oleum is used because of the high ability to disperse pristine SWCNTs and does not allow the rebundling after the end of the procedure. However, the excess of the SO_3 that is present in oleum, is responsible for the appearance of sulfonic groups on thesidewall of the CNTs [54]. This reaction produces water and alcohol soluble CNTs. A new method later appeared to produce exfoliated individually functionalized CNTs that avoids significant sulfonation of the products and does not require oleum [55]. In this case, a mixture of 96% $H_2SO_4$and ammonium persulfate known as Caro's acid is prepared, sodium nitrite is added for transforming the starting aryl amines in the intermediate diazonium salts, while 2,2'-azobis-(isobutyronitrile) (AIBN) is chosen as radical initiator. One of the "greenest" approach that has been proposed for the use of diazonium salts on CNTs, is the use of ionic liquids (ILs) as solvents [56]. The advantages of those new typology of solvents are quite well know, as they appear to besalts that are liquids at room-temperature, their boiling point is over 200 °C, they are non-volatile and can be recycled for several cycles [57]. The combination of ILs chemistry with diazonium chemistry for nanotubes produces functionalized materials in minutes at room temperature using only a mortar and pestle to mix the reactants as bigger effort.

Even if several different molecular reducing agents or simple thermal decomposition are used for activating the degradation of aryl diazonium salts and generate the radical intermediates (*i.e.* CuI), electrochemical reduction of diazonium salts is also exploited to minimize the tendency of the produced aryl radical to dimerize or subtract a hydrogen atom from the solvent [51]. This happens because the radical is created at the surface of the CNT, exactly where the reaction has to take place; moreover, the absence of other molecular species in solution, especially metallic ones, does not eventually promote side-reactions and simplifies the post-process phase.

From a mechanistic point of view, Tour *et al*. [51] purposed a possible explanation for the reaction pathway they were following that strictly derived from the classical model for the reaction or diazonium salts with aromatic substrates. The aryl radical is generated by electrochemical reduction of diazonium salts, with the presence of a molecular reductive agent. In the second step the so formed radical reacts with a sp^2 carbon on the nanotube scaffold, leaving an neighboring radical that may further react or be quenched by solvent (Fig. **6**). Another mechanistic explanation of the reactivity of diazonium compounds with CNTs has been reported in literature. McDermott *et al*. [58] proposed a polymerization growth mechanism for the reaction of HOPG with 4-nitrophenyl diazonium salts in which aryl radicals attached on the wall of the CNTs followed by the formation of a polyphenylene chain which wrapped around the nanotubes. Several proofs coming from Raman spectroscopy, TEM and AFM images have clearly proved the efficacy of the functionalization protocol in opposition to the polymer growing chain hypothesis. Later Tour *et al*. [50] propose another mechanism valid in absence of electrochemical reduction; from the presented data, they suppose that functionalization occurs when Carbon Nanotubes donate an electron to the diazonium salt, promoting the functionalization. This yields in the expected expulsion of N_2 and produces a highly active aryl radical species which then is attached on the sidewall of the tube. Lately

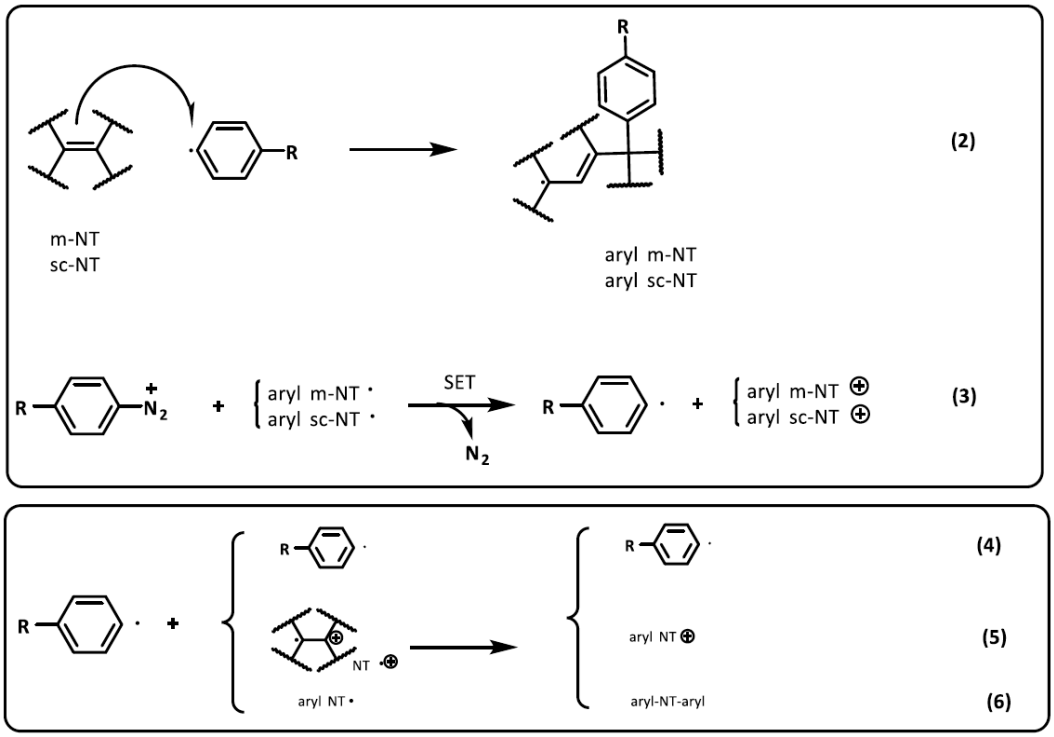

Fig. (6). Proposed free-radical chain mechanism for the reaction of diazionium with SWCNTs. (2) initiation step; (3) propagation step; (4)-(5)-(6): examples of termination steps. In the radical aryl-NT˙ structure in step (3), the radical is formed in the 1,2-position from the aryl binding site but can migrate away through the π structure of the SWCNTs.

Schmidt *et al*. [46] performed kinetic analysis for elucidating the mechanism of this reaction. Absorption spectroscopy and ESR measurements reveal a chain radical reaction, in which metallic CNTs act as catalysts. A Hammet correlation was used for the elucidation of the critical step of the selectivity. Responsible for this effect is the electrophilicity of the diazonium salts and the ratio between metallic and semiconducting SWCNTs. Based on these the functionalization and the purification can be controlled as it has been previously commented from Tour *et al*. [59] elsewhere.

In accordance to these statements, Kim *et al*. [60] used *p*-hydroxybenzene diazonium salt to functionalize only metallic SWCNTs at 45 °C. Deprotonation can take place in alkaline solution and can produce a negative charge on the functionalized SWCNTs, which can be used for electrophoretic separation. According to this simple procedure, the two main groups of the SWCNTs, metallic and semiconducting, can be separated by using the differences in electrophoretic mobility. Negatively charged SWCNTs (functionalized metallic ones) can be separated by free solution electrophoresis. Different characterization techniques confirm the separation of reacted and unreacted SWCNTs.. The electronic properties shown by metallic and semiconducting nanotubes are relevant for what concerns their use in the fields of molecular electronics, transparent conductors, and sensing [61]. For these applications, the availability of SWNTs with similar features, mainly a monodisperse band gap are essential for obtaining devices with homogeneous and reproducible performances [62].

3.2. BIRCH Reduction

Birch reaction is a brilliant example of a nearly century-old, efficient reduction of aromatic compounds, using sodium in liquid ammonia [63]. The procedure has been extensively applied to carbon nanotubes; this variant is known as 'Billups-Birch reduction'.

In particular, negatively charged anionic SWCNTs are widely used for sidewall CNTs functionalization [64]. Among several procedures, negatively charged CNTs, which can act as intermediates, are produced under classical Birch conditions. In general, the SWCNTs react with alkali metals such as lithium or sodium in liquid ammonia and yield to the reduction of the carbon nanotubes and the generation of soluble CNTs anions [19e]. Firstly, was reported the Birch-like reduction of SWCNTs in 1998, by Chen *et al*. [65], by using lithium. They describe to carry out the reactions under two different conditions: (a) refluxing ammonia solution, and (b) in ethylenediamine solution. The latter reaction conditions led to the incorporation of nitrogen into the sample and were no further investigated.

Pekker *et al*. [66] reported prepared hydrogenated SWCNTs and MWCNTs with the use of Birch reduction. The morphology of the hydrogenated CNTs was examined by spectroscopy techniques and concluded into considerable structural changes. While the pristine material consisted of straight parallel walls, the hydrogenated one showed extended corrugation and partly disorder through the whole sample, including the inner walls. The amount of hydrogen which is attached on the SWCNTs, after lithium-ammonia hydrogenation, was also calculated from TGA/MS and corresponded to a composition of $C_{11}H$.

A very recent work by Hof *et al*. [67] describes the synthesis of brominated carbon nanotubes, with the use of reductive bromination procedure, in which the first step involves a Birch type reduction in liquid ammonia. The so formed brominated SWCNTs can lead to the formation of hydroxylated SWCNTs derivatives, after the nucleophilic substitution of bromine moieties from water molecules. This study purposes an interesting and efficient route to obtain hydroxylated SWCNTs, as a highly reactive platform for further decoration of the nanomaterial with different organic moieties.

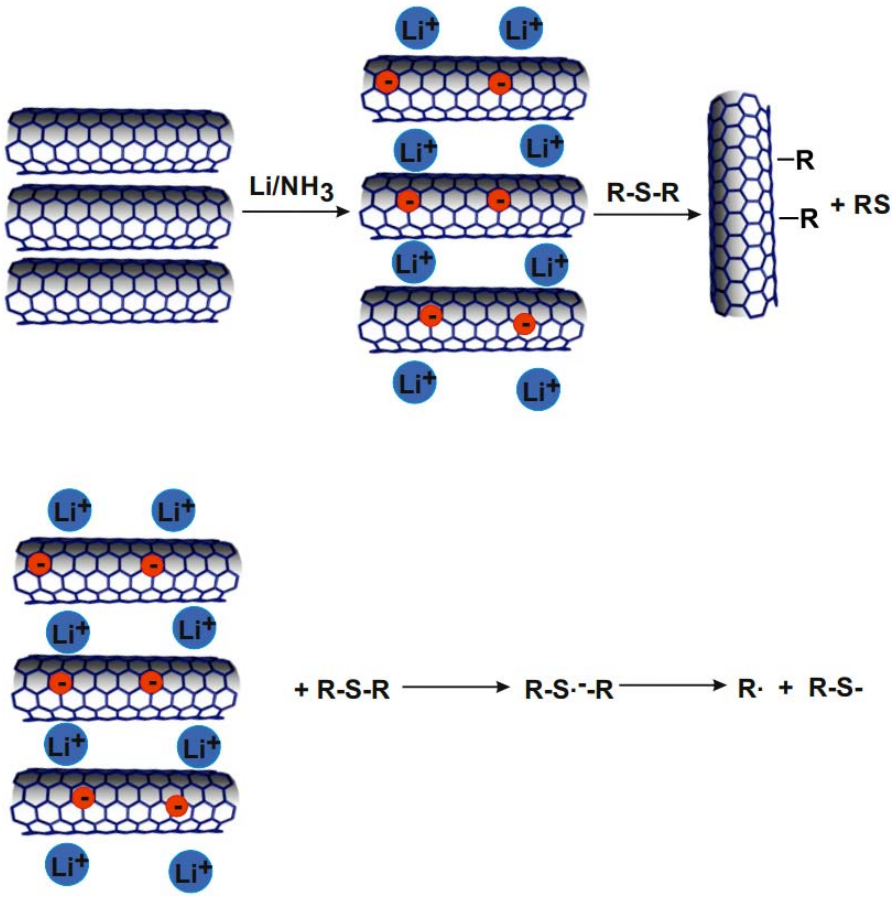

Fig. (7). Reaction mechanism scheme for Single Electron Transfer (SET) pathways.

In 2004, Billups and coworkers [68] first reported a sequence to functionalize single-wall carbon nanotubes without the use of sonication *via* reductive alkylation. They solubilized lithium in liquid ammonia and inside this mixture were added the CNTs, followed by stirring and finally by the addition of alkyl halides [69]. The so-called 'Billups reaction' has been successfully applied also to MWCNTs [70] and DWCNTs [71]. In 2007, they further demonstrated that carbon nanotube salts dispersed in liquid ammonia participate in reactions involving a single electron transfer (SET) to alkyl or aryl sulfides to yield SWCNTs functionalized by alkyl or aryl groups (Fig. **7**). They also established that carbon nanotubes can be functionalized by sulfur-centered free radicals *via* the SET mechanism using disulfides in a lithium/liquid ammonia medium [72].

A two-step reductive alkylation of SWCNTs introduces two different groups on the SWCNTs showing notable effects on the amount of the substituents. The number of the attached groups can be controlled by the alkyl group of alkyllithium and alkyl halide as described by *Maeda* and coworkers [73]. An accurate study on the propagation mechanism of reductive alkylation has been recently reported in literature. Deng *et al*. [74] demonstrate through SEM imaging that the reaction takes place on SWCNTs by activation of sp^3 defect sites; it's worthy to mention the work appeared in 2006 from Liang, *et al*. [75], in which SWCNTs are reduced to radical species which are directly employed for in situ polymerization of methyl methacrylate. The protocol, simple and scalable, does not require ultrasound irradiation for the initial de-bundling of pristine tubes and can be applied for functionalizing CNTs with a variety of vinyl-based polymeric materials.

In the recent time, a novel synthetic procedure for SWCNTs covalent modification with a variety of nucleophilic agents is developed, through Birch hydrogenation which is followed by epoxidation [76]. Inasmuch the low reactivity of CNTs is related to their graphitic structure, Birch reduction is useful to transform, the nature of the SWCNTs from sp2 carbons to sp3 ones. Such an alteration has as a consequence the enhanced reactivity in the reaction characteristics of olefins, *e.g*. epoxidation.

Similarly to oxidative pathways, reduction protocols can be applied for the insertion of carboxylic groups, and is proceeded through radical intermediates. From a conceptual point of view, the obtaining of -COOH moieties can arise from oxidation of a C-atom provided from the same nanotube surface or directly from the electrophilic addition of CO_2 to opportunely pre-treated nanotubes. Some early attempts in this direction were provided by Chen *et al*. by the use of *s*-Bu Li and carbon dioxide, even if low functionalization degree was reported [77].

In 2010 and 2011 Gebhardt *et al*. [78] reported a so-called 'modified Birch reduction' procedure, a more effective protocol with controlled addition of different carbonyl compounds [79] and with amounts of a CO_2 addition. The control over the amount of the attached chemicals' groups took place by the use of different reaction conditions (reaction time, pressure, etc.) [78], suggesting the substitution of ammonia with THF as solvent. In such a procedure, SWCNTs are dispersed by sonication in dry THF. In this mixture are added the liquid ammonia and the lithium metal. Subsequently, the ammonia is evaporated and the formed lithium bronze removed, letting a stable black dispersion compared to oxidative treatments, in this case the nanotubes undergo to reduction and localize nega-

tive electronic density over the surface and, after single electron transfer processes from the tubes to CO_2, yielding to the formation of radical anions $CO_2^{-\bullet}$. Afterward, they attack the sidewall of SWCNTs, in a way similar to the alkyl and aryl iodides addition as described by Billups *et al*. [72, 80]. This procedure, followed by alkylcarboxylation, shows high degree of functionalization and high selectivity in the following order: small semiconducting SWCNTs, large semiconducting SWCNTs and small metallic SWCNTs [81]. In contrast, in the 'classical' Birch reduction the selectivity is towards the metallic SWCNTs [82].

Alternatively, Engtrakul *et al*. [83] use sodium naphthalide to reduce the SWCNTs in THF and yield in highly hydrogenated tubes. THF except the role of the solvent is also the hydrogen source.

The use of reduced nanotubes and the CO_2 as electrophile can yield to carboxylic acid moieties on the sidewall without the destruction of the σ-framework [77].

Previous attempts with CO2 as electrophile, like the classical Birch reduction [78] or the use of *sec*-butyl lithium as reductant s [77] give low amount of substitution of the scaffold of the CNT.

An interesting application of Birch reduction of CNTs is in the field of electrodes. Advanced architectures to achieve the new-generation lithium ion batteries has been reported. The electrochemical properties of the Co_3O_4-CNTs heterostructures as anode materials for lithium ion batteries are investigated. Modified Birch reduction is used for the decoratation of CNTs with alkylcarboxyl group. . Co_3O_4 is formed in situ on te functionalized CNTs. [84].

Even if the concept is slightly different, radical protocols have been reported for the introduction of carboxylic groups over nanotubes surface with a variable length organic connectors; in these reactions, a ω-bromocarboxylic acid reacts with carbon nanotubes following a Billups-Birch reductive mechanism in which the radial anion formed over the surface of the tubes is able to give substitution of the halogen atoms over the carboxylic acid reagent. The resulting water soluble nanotubes are in general well dispersed and notably soluble (up to 3.38 mg/mL) [71].

3.3. Carbene Addition

One of the first successful sidewall functionalizations of Carbon Nanotubes is the use of carbene derivatives [85]. In these cases either shortened SWCNTs or pristine ones are being used [85b]. As a reactive agent is used $PhHgCCl_2Br$ which is decomposed in solution under heating, forming dichlorocarbene that is able to attack the scaffold of the SWCNTs. The functionalization of CNTs with carbenes was further supported by theoretical calculations. In these works the stability of the carbene moieties on the nanotubes was investigated [86]. In addition these calculations reveal that this cycloaddition type of reaction is site selective on the nanotubes [86b]. Further investigation was held on the functionalization of MWCNTs [87].

The latest works on this type of reaction consider the synthesis of hybrid materials and the effect on the electronic properties of CNTs. In the work of Ismaili *et al*. [88] was used a diazirine compound bearing a terminal free thiol group. The use of the light allows the *in situ* carbene formation with the release of nitrogen, followed by addition on the CNTs. On the other hand, the thiol group is exploited for grafting on Au nanoparticles. This approach is very useful to providea robust AuNP-CNT nanohybrid system.

This type of functionalization, deeply explored byLiu *et al*. [89] and Zhang *et al*. [90] showed to influence the electric properties of the CNTs and also to be a diameter selective. It was indeed reported that the metallic character of the metallic SWCNTs remains unaffected while the semiconducting SWCNT transformed into metallic upon carbene functionalization reaction. This occurred due to the carbene-based functionalization which results in different interfacial bonds on metallic and semiconducting SWCNTs. For the metallic SWCNTs the sp^2 nature of the bond is preserved while for the semiconducting ones the bond is rehybridized to sp^3 type. In addition, this functionalization procedure is more in favor of the small diameter SWCNTs than of the larger ones [90].

4. DISULFIDES

Sulfur-containing nanomaterials are noticeable between the scientific community because of their unique properties which are derived from sulfur atoms. Cyclic disulfides are photolysed easily to give α,ω-alkyldithio radicals [91].

Nakamura *et al*. [92] reported a method for sidewall modification of SWCNTs, which is based on photolysis of cyclic disulfides. In a typical experiment, cyclic disulfides and SWCNTs were irradiated through mercury lamp for 7 h at r.t. The addition of the sulfur-containing substituents was confirmed by Raman, XPS, FT-IR, mass and UV measurements. They further demonstrated to attach with gold nanoparticles on sidewall sulfur-containing SWCNTs. In 2013, Syrgiannis *et al*. [93] reported a detailed examination on a novel, atom economical, one step and reliable protocol for nanotube functionalization with aliphatic and aromatic disulfides, through heating for 48 hours at reflux in toluene. Furthermore, were investigated cystamine dendrimers of different generations as adducts and obtained SWCNTs with high degree of functionalization (Fig. **8**).

Functionalization of CNTs with sulfur atoms remains an exotic protocol, but it appeared only recent and in any case it proofs that scientific community is still active in the search of new chemical strategies for nanotubes functionalization and in the near future it's possible that novelties will arrive in this field.

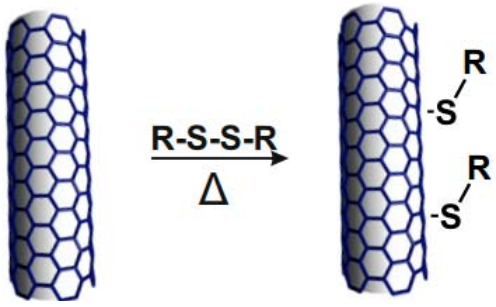

Fig. (8). The addition of disulfides on SWCNTs.

5. POLYMER GRAFTING

Epoxy groups grafted on CNTs are the materials which are used more for improving the interface of nanocomposites in load transfer. The ring-opening reaction of the epoxy groups can yield into different kinds of functionalities. This ring-opening reaction provides materials which can be used for applications in the composite materials, polymer surface modification and membrane technology [94]. Moreover, the epoxy group can be involved in cross- linking reactions with amines, carboxylic acids, anhydrides and hydroxyl-containing polymers, making the materials attracting for the use in different devices [95 40b].

The anchorage of polymeric chains to nanotubes can provide a better solubilization of the tubes in the polymeric matrix which will

incorporate them, or otherwise the polymeric pendants can help dispersion of nanotubes depending from their own characteristics. Further chemistry can be performed if polymers bear specific groups which remain unmodified after the polymerization process over the tubes surface.

In 2003 first protocols concerning radical functionalization of CNTs with polymeric materials appear in the literature. All of these works have in common the same logical approach towards the lack of solubility of the nanotubes or their inert character. Grafting processes are characterized by the employ of polymers as functionalization agents. It's possible to directly attach chains onto the tubes in one step, or perform the in situ polymerization so that the attachment of the first pendants to the tubes structure can be followed by the growth of the polymeric chains.

One of the first successful reported examples is the work of Kong *et al*. [96] in which atom transfer radical polymerization (ATRP) approach is employed for the functionalization of MWCNTs (Fig. **9**). The novelty of this method was due to the fact that (i) the co-polymer could be grown directly in situ using the monomeric units as raw materials, and (ii) the functionalization degree can be easily modulated before the polymerization process since the reacting sites are the carboxylic groups previously attached onto pristine material (see paragraph before) and remain constant after the graft polymerization and purification of the products. The synthetic strategy can be summarized in 5 passages: (i) preparation of oxidized MWCNTs with 60% HNO_3, (ii) transformation of the carboxylic groups in the more reactive carbonyl chlorides using thionyl chloride, (iii) introduction of a spacer (short glycol chain) bearing hydroxyl-moieties, (iv) ATRP in presence of 2-bromo-2-methylpropionyl bromide, and (v) grafting polymerization of methyl methacrylate (MMA) by means of in situ ATRP. The possibility of precise control of polymer layer thickness by tuning the feed ratio (in weight) of MMA to the precursor produced in passage (iv) allowed to export the method to other reactions where surface morphology/thickness are crucial factors in the application which the material is designed for.

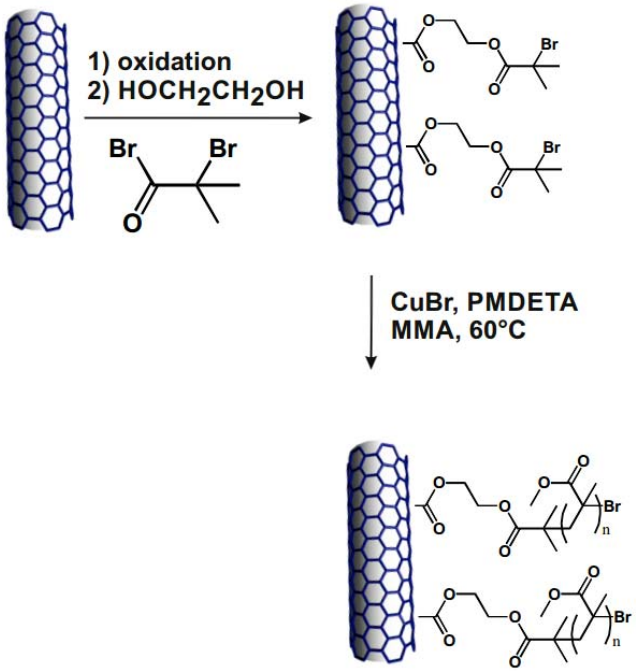

Fig. (9). Functionalization scheme followed by Kong *et al*. [96] in their polymer grafting approach.

Similarly, Qin *et al*. [97] worked on SWCNTs to bypass the chronical absence of solubility of pristine materials in organic solvents. In their approach, oxidized SWCNTs were used and ATRP occurs in presence of poly(n-butyl methacrylate) (PnBMA), after transformation of carboxylic moieties in acyl chlorides and the anchorage of the polymerization initiator, 2-hydroxyethyl-2'-bromopropionate (HEBP). The reported solubility of these materials strongly correlates with the amount of the grafted polymer. Functionalized SWCNTs which contain 22% PnBMA and 78% SWCNTs-initiator disperses well in *o*-DCB as a black suspension for 2 days before noticeable aggregation occurs but precipitates from chloroform and THF in a few hours. On the other hand samples that contain 40% PnBMA and 60% SWCNT-initiator form a solution in *o*-DCB and flocculates after a few days in chloroform and THF. The highest conversion sample reported, which contains 57% PnBMA and 43% SWCNT-initiator, is stable for weeks as black solutions in *o*-DCB, chloroform, and THF.

Lately Sun *et al.* [98] exploit the approach for the preparation of modified aligned carbon nanotubes (AIBN). The preparation of responsive materials easy to get integration in micro-devices is a technological field of great interest and aligned nanotubes can be one of the most promising candidates, but their well-known superhydrophobicity has to be bypassed [99]. ATRP allowed to functionalize the nanotubes film through linkage of poly(N-isopropylacrylamide) (PNIPAAm). Such a method can be easily extended to other polymeric species allowing a precise control of the surface properties or the interaction with biomolecules, in the case of applications in sensor technology.

Li *et al*. [100] report another interesting application of nanotube-based materials for technological application; for reaching high performance in alkaline fuel cells, an intimate incorporation of functionalized carbon nanotubes was requested to improve both ionic conductivity and mechanical properties of alkaline polymer electrolyte membranes (Fig. **10**). Thus, the answer had been to integrate the solvent molecules directly into the nanotubes. The strategy was to functionalized multi-walled carbon nanotubes with an imidazolium-type ionic liquid polymer *via* in situ free radical polymerization of 1-vinyl-3-methyl-imidazolium iodide ([VMIm][I]) and then blended with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) containing imidazolium groups in solution to fabricate composite membranes. It was demonstrated that the incorporation of the PIL(BF_4)-MWCNTs into the membranes of PPO can increase both conductivity and mechanical properties. The composite membrane containing 0.3 wt% of PIL(BF4)-MWCNTs exhibits a dramatic enhancement in ionic conductivity (95.3%) and tensile strength (82.9%) in comparison to the membrane without PIL(BF4)-MWCNTs. This experimental evidence demonstrates that the incorporation of functionalized carbon nanotubes is a useful strategy for improving both ionic conductivity and mechanical properties of alkaline polymer electrolyte membranes.

An application destined to environmental chemistry is proposed from Liu *et al*., [101] regarding multi-walled carbon nanotubes functionalized with amphiphilic-copolymer of poly(sulfone) (PSF) and poly(sulfobetaine methacrylate) (PSBMA). ATRP techniques were used for the functionalization of the nanotubes and production of protein-resistant PSF-based nanocomposite films. The PSF-based nanocomposite films exhibit about 4.4% fibrinogen adsorption compared to that of the PS Petri dishes, and 3.6% compared to that of to the bare silicon wafer surfaces. The membrane made of PSF/MWCNT-PSF/PSBMA nanocomposite also exhibits antifouling characteristics in BSA ultrafiltration experiments. The results

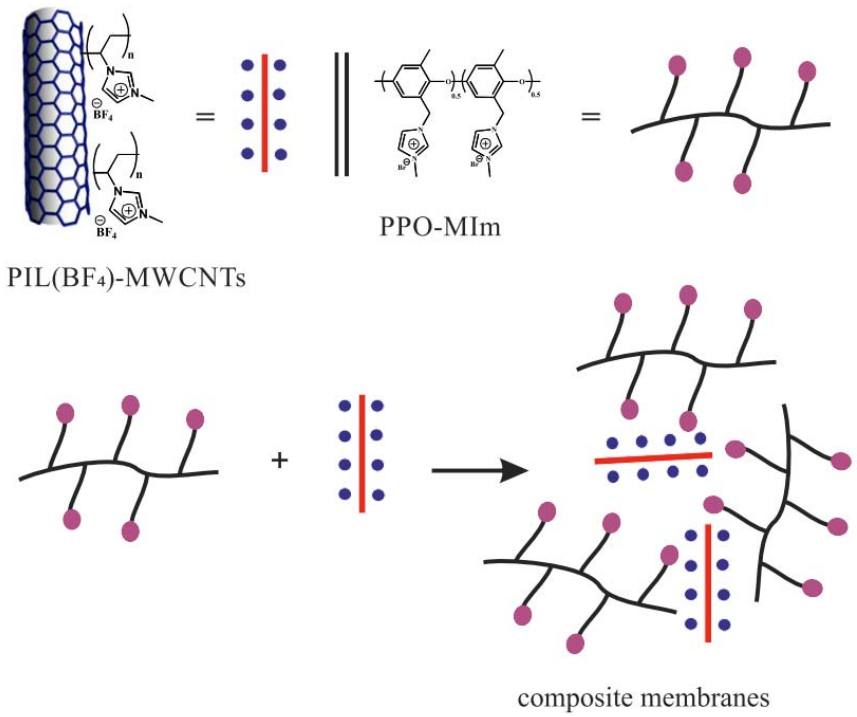

Fig. (10). Synthesis of PIL(BF_4)-MWCNTs, PPO-MIm and composite membranes (modified from reference [100]).

demonstrate a convenient and effective approach to the preparation of low-protein adsorption surfaces and antifouling membranes. Applications of the synthetized nano-composites for the marine biofouling-resistant materials are of great interest and under investigation.

Finally, Joo *et al.* [102] produced CNTs-based novel nano-drugs. In their work, MWCNTs are grafted from poly[2-(dimethyl-amino)ethyl methacrylate] (PDMAEMA), and they show antibacterial effect against E. coli as well as S. aureus. It was shown that the loss of viability of E. coli highly depends on the PDMAEMA content in the PDMAEMA-functionalized MWCNT. The highest viability loss achieved in this study was 42% with the PDMAEMA-functionalized MWCNTs containing 53.9 wt.% of PDMAEMA.

CONCLUSION

Chemistry always evolves in the direction of new strategies to be performed over existing materials in order to improve their features or create materials with radically different properties. Carbon Nanotubes chemistry is one of this example for different reasons: (i) the necessity to modulate CNTs properties (solubility as first) in order to render them easier manipulated, (ii) the continuous demand of new high performance materials for which CNTs appear to be one of the best candidates since there is the possibility to manipulate a material that, in the pristine form, possess extraordinary properties. Radial reactions are an attractive way for changing the nanotubes' properties and render them more prompt for further manipulation. Among the vastness of literature produced on this topic, some protocols are more flexible and diffused than others. Oxidation strategies are ubiquitous because several protocols for the introduction of alkyl pendants require reactive sites that can be introduced necessarily from an oxidative reaction. Radical/nucleophilic addition (*i.e.* diazionium salts reaction and Birch reaction) have the advantage of simplicity, flexibility and are suitable for a fine tuning of functionalization degree of the final material. Without any doubt, the number of different possible applications in which radical protocols can be employed is impressive and further research in this field is mandatory.

LIST OF ABBREVIATIONS

AFM	=	Atomic Force Microscopy
AIBN	=	2,2'-azobis-(isobutyronitrile)
ATRP	=	atom transfer radical process
BET	=	Brunauer-Emmett-Teller
CNTs	=	Carbon Nanotubes
DSSC	=	dye-sensitized solar cell
DMF	=	dimethylformamide
DWCNTs	=	Double-Walled Carbon Nanotubes
ESR	=	Electronic Spin Resonance
FETs	=	field effect transistors
HEBP	=	2-hydroxyethyl-2'-bromopropionate
HOPG	=	highly ordered pyrolytic graphite
ILs	=	ionic liquids
LEDs	=	light emitting diodes
m-CPBA	=	m-chloroperbenzoic acid
MMA	=	methyl methacrylate
MWCNTs	=	Multi-Walled Carbon Nanotubes
o-DCB	=	*o*-dichlorobenzene
PDMAEMA	=	poly[2-(dimethylamino)ethyl methacrylate]
PnBMA	=	poly(n-butyl methacrylate)
PNIPAAm	=	poly(N-isopropylacrylamide)
PPO	=	poly(2,6-dimethyl-1,4-phenylene oxide)
PSBMA	=	poly(sulfobetaine methacrylate)
PSF	=	poly(sulfone)
SEM	=	Scanning Electron Microscopy

SWCNTs	=	Single-Walled Carbon Nanotubes
TEM	=	Transmission Electron Microscopy
TFDO	=	methyl(trifluoromethyl)di-oxirane
THF	=	tetrahydrofuran
[VMIm][I]	=	1-vinyl-3-methyl-imidazolium iodide

CONFLICT OF INTERESTS

The authors declare that this article content has no conflicts of interest.

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